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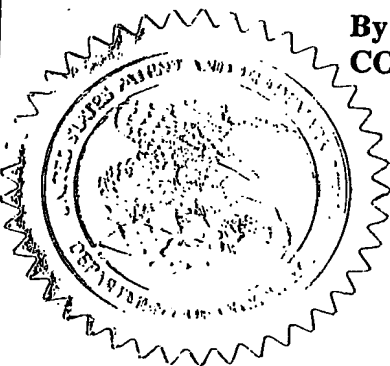
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Docket No. 3174

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

## PROVISIONAL APPLICATION COVER SHEET

## BOX PROVISIONAL PATENT APPLICATION

Hon. Commissioner for Patents  
Washington, DC 20231J1046 U.S. PTO  
60/441516  
01/21/03

Sir:

(A) The attached document is filed as a PROVISIONAL APPLICATION for patent under 37 CFR 1.53 (c)(1).

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(C) Title: NONMETALLIC SULPHUR-FREE BASIC LUBRICANT ADDITIVE COMPOSITION AND LUBRICANT COMPOSITION THEREOF

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(E) Docket No. 3174

(F) Send Correspondence to: Docket Clerk

Patent Department, Drop 022B

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(G) Fees: Charge the fee for filing of a provisional application, believed to be \$160.00, to deposit account 12-2275 (The Lubrizol Corporation). Any deficiency or overpayment in fees should be charged or credited to the same account.

(H) Contains: 7 pages of Specification and 1 page of claims.

(I) A duplicate of this Cover Sheet is attached.

Respectfully submitted,  
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I certify that this correspondence is being deposited with the United States Postal Service as express mail in an envelope addressed to: Assistant Commissioner for Patents, Box Provisional Patent Application, Washington, DC 20231, on:

Jan. 21, 2003

Express Mail # EU 38134974 USBy: Shirley E. KellyDate: 1/21/03

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TITLE: NONMETALLIC SULPHUR-FREE BASIC LUBRICANT ADDITIVE  
COMPOSITION AND LUBRICANT COMPOSITON THEREOF

FIELD OF THE INVENTION

This invention involves a nonmetallic sulphur-free lubricant additive composition that has a total base number, a lubricant composition containing the lubricant additive composition, and methods involving the lubricant additive composition and the lubricant composition. The lubricant additive composition is useful in providing detergency and dispersancy performance to a lubricant composition such as an engine oil without adding sulphur or metals to the lubricant composition.

BACKGROUND OF THE INVENTION

Detergents are lubricant additive compositions that typically provide detergency performance to a lubricant composition that can include neutralizing acids, preventing corrosion, and providing cleanliness by suspending deposit forming substances and removing deposits. Detergents generally consist of an anionic organic surfactant portion that usually contains sulphur such as an alkylarylsulfonate, a cationic metal counterion, and a basic metal salt in a colloidal suspension that provides a base reserve for neutralizing acids. Various lubricant compositions such as certain two-stroke engine oils and stationary natural gas engine oils require detergency performance, but also require that the engine oil contain little or no metals for satisfactory performance. Current and future regulations regarding exhaust emissions from internal combustion engines that contain exhaust treatment devices are requiring a reduction in the sulphur, phosphorus and metal content of engine oils used in these engines. This reduction in the sulphur, phosphorus and metal content of engine oils is being implemented because it is thought that they can adversely affect the performance of exhaust treatment devices. Dispersants provide cleanliness to all types of lubricant compositions by suspending deposit forming substances.

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It has now been found that the lubricant additive composition of the present invention provides detergency and dispersancy performance to a lubricant composition such as an engine oil and is free of sulphur and metals.

#### DETAILED DESCRIPTION OF THE INVENTION

A lubricant additive composition of the present invention comprises a reaction product of (a) a member selected from the group consisting of (1) an alkyl-substituted, carboxyl-substituted phenol; (2) an oligomeric reaction product of an alkyl-substituted phenol and an aldehyde; and (3) an oligomeric reaction product of an alkyl-substituted phenol, an aldehyde, and a carboxyl-substituted phenol; and (b) an organic nitrogen-containing base selected from the group consisting of (1) an amino-containing imine or a reactive equivalent thereof; (2) ammonia or a reactive equivalent thereof; and (3) a tetraalkylammonium hydroxide or a reactive equivalent thereof wherein the lubricant additive composition has a total base number and is free of sulphur and metals.

The alkyl substituent of the alkyl-substituted, carboxyl-substituted phenol of the reactant (a)(1) can be derived from an olefin or a polyolefin. The polyolefin can be prepared from ethylene, propylene, or a butylene such as isobutylene. The olefin or polyolefin can have 4 to 50 carbon atoms, 6 to 40 carbon atoms in a second instance, and 7 to 30 carbon atoms in a third instance. The alkyl-substituted, carboxyl-substituted phenol can be an alkyl-substituted salicylic acid which is commercially available or can be prepared by well known methods such as via the Kolbe-Schmidt reaction of carbon dioxide with an alkali metal phenolate salt.

The alkyl substituent of the alkyl-substituted phenol of reactant (a)(2) can be derived from an olefin or polyolefin as described above for the alkyl substituent of the alkyl-substituted, carboxyl-substituted phenol of reactant (a)(1). The alkyl-substituted phenol of reactant (a)(2) is readily prepared from phenol and an olefin or polyolefin by well known alkylation methods. The aldehyde of reactant (a)(2) can be formaldehyde or a reactive equivalent thereof such as formalin or paraformaldehyde. The oligomeric reaction product of the alkylphenol and aldehyde in reactant (a)(2) can be prepared in the presence of an acid catalyst, a base catalyst, or a stoichiometric amount of a metal base as described in U. S. Patent No. 3,256,183 to give a metal salt

of the oligomeric reaction product. This metal salt of the oligomeric reaction product can be converted to non-ionic, metal free compound by treating it with an acid to remove the metal.

The alkyl substituent of the alkyl-substituted phenol of the reactant (a)(3) can have 1 to 60 carbon atoms, in another instance 5 to 50 carbon atoms, and in a further instance 7 to 40 carbon atoms. The alkyl substituent can be derived from an olefin. The alkyl substituent is typically derived from a polyolefin which can be a homopolymer from one olefin monomer or a copolymer from a mixture of two or more olefin monomers. The olefin monomer can be an alpha-olefin, an internal olefin, or a polyene and includes ethylene, propylene, butene isomers, pentene isomers, decene isomers, and dienes. Useful polyolefins are polypropylenes and polyisobutylenes. Methods to prepare the polyolefins and the alkylphenols via alkylation of phenol with olefins or polyolefins are well known. The aldehyde of the reactant of (a)(3) can have 1 to 6 carbon atoms. The aldehyde can be formaldehyde in one of its reactive forms such as formalin or paraformaldehyde. The carboxyl-substituted phenol of the reactant of (a)(3) can be a 2- or 3- or 4-hydroxybenzoic acid which can have alkyl substituents. A useful carboxyl-substituted phenol is salicylic acid. The reactant product of (a)(3) contains at least one alkyl-substituted phenolic unit and at least one carboxyl-substituted phenolic unit. The reactant of (a)(3) can contain 2 to 20 phenolic units, 2 to 10 phenolic units, or 2 to 8 phenolic units. The reactant of (a)(3) can include linear molecules, cyclic molecules, or mixtures thereof. In an embodiment of the invention the reactant of (a)(3) is a mixture of linear and cyclic molecules, and in another embodiment the mixture contains a majority of linear molecules. The reactant of (a)(3) can be prepared as described in U. S. Patent No. 6,200,936 and Example 1 hereinbelow using a basic catalyst and a solvent. Basic catalysts include alkali and alkaline earth metal bases and amines such as lithium hydroxide, sodium hydroxide, potassium hydroxide and ammonium hydroxide. A solvent can be employed in the preparation of the reactant of (a)(3) up to 90% by weight of the reaction mixture. The mole ratio of the alkylphenol to the carboxyl-substituted phenol can range from 1:0.05 to 1:19, and in a further embodiment of the invention is about 2 alkylphenols to 1 carboxyl-substituted phenol. The mole ratio of combined alkylphenol and carboxyl-substituted phenol to aldehyde can be 1:0.5-3.

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The organic nitrogen-containing base of the present invention can be (b)(1) an amino-containing imine or reactive equivalent thereof. The amino-containing imine can be guanidine, aminoguanidine, or acetamidine. Reactive equivalents of this imine can be salts of the imine with acids to include hydrogen chloride, carbonic acid, and carboxylic acids such as formic acid and acetic acid. Examples of reactive equivalents of the imines are guanidine carbonate, aminoguanidine bicarbonate, and acetamidine hydrogen chloride.

The organic nitrogen-containing base can be (b)(2) ammonia or a reactive equivalent thereof which can be a salt of ammonia with acids to include water, hydrogen chloride, carbonic acid, and carboxylic acids such as formic and acetic acid.

The organic nitrogen-containing base can be (b)(3) a tetraalkylammonium hydroxide or reactive equivalent thereof that can be a tetraalkylammonium salt containing as the anionic counterion chloride, carbonate, bicarbonate, or a carboxylic acid anion such as formate or acetate.

The reaction product of the present invention of reactants (a) and (b) can be prepared by heating the reactants at about 50 to 200°C, in a second instance at about 60 to 175°C, and in a third instance at about 70 to 150°C. The reaction can be run using a lubricating oil as a diluent. The reaction can be run in the presence of a solvent to include water, alcohols, and aliphatic and aromatic hydrocarbons. A method to prepare the lubricant additive composition of the present invention from reactants (a) and (b) is described in Example 2 hereinbelow.

In an embodiment of the present invention a lubricant composition comprises a lubricating oil and the lubricant additive composition of the present invention. The lubricating oil can be a natural oil, synthetic oil, or mixture thereof. Natural oils include animal oils, vegetable oils, and mineral oils from various sources. Synthetic oils include esters of carboxylic acids, poly(alpha-olefins), and polyalkylene glycols. The lubricant composition can further contain other lubricant additives to include nitrogen-containing dispersants such as polyisobutenylsuccinimides, neutral and overbased metal-containing detergents such as a calcium overbased alkylarylsulfonate, antioxidants such as alkylated diarylamines, antiwear agents such as dialkyl dithiophosphates, friction modifiers, and antifoaming agents. In an embodiment of the invention the lubricant composition contains the lubricant additive

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composition of the present invention, and in other embodiments the lubricant composition contains a mixture of the lubricant additive composition and a metal-containing detergent, a mixture of the additive composition and a dispersant, and a mixture of the additive composition and a metal-containing detergent and a dispersant. The lubricant additive composition of the present invention can be present in a lubricant composition alone or in a combination with a metal-containing detergent in an amount that provides satisfactory detergency performance for the lubricant composition. The lubricant additive composition can be present in a lubricant composition alone or in a combination with a dispersant in an amount that provides satisfactory dispersancy performance for the lubricant composition. The lubricant additive composition can be present in a lubricant composition at about 0.5 to 40% by weight, at about 0.75 to 20% by weight in another embodiment, and at about 1 to 15% in a further embodiment.

In a method of the present invention the lubricant additive composition of the present invention is prepared by reacting the reactants (a) and (b) of the present invention at an elevated temperature of about 50 to 200°C, at 60 to 175°C in a second instance, and at 70 to 150°C in a third instance.

In another embodiment of the present invention a method of providing detergency performance to an internal combustion engine comprises lubricating the engine with a lubricant composition that contains the lubricant additive composition of the present invention wherein the additive composition is free of sulphur and metals. In a further embodiment of the present invention a method of providing detergency and dispersancy performance to an internal combustion engine comprises lubricating the engine with a lubricant composition that contains the lubricant additive composition of the present invention wherein the additive composition is free of sulphur and metals. The internal combustion engine can be a spark-ignited or a compression-ignited engine. The engine can contain an exhaust treatment device. The lubricant composition for the engine can be an engine oil that has a reduced level of sulphur, phosphorus, metal, or mixtures thereof. The sulphur content in the engine oil can be below 0.5% or 0.3% or 0.2% by weight. The phosphorus content in the engine oil can be below 1% or 0.08% or 0.05% by weight. The metal content in the engine oil expressed as a sulphated ash can be below 1.5% or 1.2% or 1% by weight.

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### Example 1- PIB phenol-formaldehyde-salicylic acid

A 2 liter reaction flask was charged with 475 g polyisobutenyl (PIB, 550 number average molecular weight, GLISSOPAL® 550 from BASF) substituted phenol (0.739 mole, 1 eq) and 330 g mineral oil (SN150) and heated to 30°C. Via a pressure equalizing dropping funnel, 3.4 g of 50% aqueous KOH (0.030 mole, 0.04 eq) was added all at once. The materials were heated to 75°C followed by addition over 0.5 hour via a pressure equalizing dropping funnel, 81.6 g 37% aqueous formaldehyde (formalin) (1.01 moles, 1.367 eq) followed by heating at 75°C for 2 hours until free formaldehyde measured less than 2% (by titration). To the reaction was charged 51.6 g salicylic acid (0.374 mole, 0.51 eq) and the reaction was heated to 140°C as quickly as possible (0.3 hour) while controlling reflux, draining water of reaction via a Dean Stark trap. The reaction was held at 140°C for 1.5 hours while collecting 58 ml water. The materials were vacuum stripped at 140°C/100 mm Hg over 0.5 hour. The clear and golden residue was the product. Yield = 857 g, % K = 0.093%. Mass spec, GPC and  $H^1$  and  $C^{13}$  NMR indicated that the product consists of 2 methylene bridged polyisobutenyl phenol molecules methylene bridged to one salicylic acid.

### Example 2- PIB phenol-formaldehyde-salicylic acid and aminoguanidine bicarbonate

To a 1 litre flask, equipped with overhead stirrer and paddle, heating mantle, splash head, Dean-Stark trap and condenser equipped for water removal, pressure equalizing dropping funnel, thermocouple and thermal control unit, was added 450g of Example 1 (60% actives, 0.186moles, 1 equivalent) and 70g of toluene. This was then heated to 85°C, at which point a slurry of aminoguanidine bicarbonate (38g, 0.28moles, 1.5 equivalents) and distilled water (80g, about 90°C to aid solubility in the slurry) was added slowly over 15 minutes via a pressure equalising funnel. The reaction turned cloudy. Water removal was observed almost instantaneously after addition of the slurry. The mixture was heated in 5°C stages to 130°C. The reaction was then held for 2 hours at 130°C under reflux. Solution cleared at this point.

Whilst warm, filtered the product under vacuum through a pad of finely divided diatomaceous earth using a Buchner flask.

Sulphated ash= 0.34%

TBN= 29 mg KOH/g sample

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Kinematic Viscosity @ 100°C= 391cSt

Nitrogen= 2.9%

Dispersant Dilution Test<sup>1</sup>:

Example 1= 6

Example 2= 125

<sup>1</sup> Results are reported as a sludge to chemical ratio which represents the lowest concentration of chemical to suspend an artificial sludge in an oil solution as described in U. S. Patent Nos. 4,146,489 and 5,814,586. Higher values for the ratio indicate that a chemical is more effective in suspending sludge.

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What is claimed is:

1. A lubricant additive composition, comprising: a reaction product of
  - (a) a member selected from the group consisting of (1) an alkyl-substituted, carboxyl-substituted phenol; (2) an oligomeric reaction product of an alkyl-substituted phenol and an aldehyde; and (3) an oligomeric reaction product of an alkyl-substituted phenol, an aldehyde, and a carboxyl-substituted phenol; and
  - (b) an organic nitrogen-containing base selected from the group consisting of (1) an amino-containing imine or a reactive equivalent thereof; (2) ammonia or a reactive equivalent thereof; and (3) a tetraalkylammonium hydroxide or a reactive equivalent thereof, wherein the lubricant additive composition has a total base number and is free of sulphur and metals.

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